УДК 539.21: 621.79 DOI:10.30837/rt.2025.4.223.21

D.V. SLIUSAR, O.M. CHUGAI, I.V. KOLODIY, S.V. OLIYNYK, O.O. POLUBOIAROV, Y.A. VOLOSHYN, S.M. KULISH

COMPOSITION, STRUCTURE AND MICROHARDNESS OF MULTICOMPONENT TUNGSTEN CARBIDE BASED COATINGS FORMED USING THE INVERSE MAGNETRON SPUTTERING SYSTEM

Introduction

Composition of crystalline materials is known to be one of the factors determining their physical properties. Therefore, it is not surprising that in recent decades there has been a sharp increase in interest in multicomponent materials. A special place among such materials is occupied by high-entropy alloys (HEAs) containing five or more components [1]. This feature of the composition, causing distortions of the crystal lattice, has a significant influence on many physical properties of materials, especially mechanical ones. For this reason, early studies of VPPs were mainly devoted to their mechanical properties [2]. However, in recent years, the range of problems related to the creation of new materials of this type has significantly expanded. Accordingly, prospects for their wider practical application have emerged.

One of the promising practical applications of these alloys is related to the creation of highly efficient thermoelectric energy converters [3-5]. It should be noted in this connection that the existence of a fundamental possibility to change the material structure, the solubility limit of specific elements in it, as well as thermal and electrical properties by varying the composition has served as a basis for the introduction of a new term "entropic materials engineering" [3].

Additional opportunities for controlling the thermal and electrical properties of HESs arise when semiconductor compounds are used for their creation. Thus, it was shown in [4] that the optimal combination of thermal and electrical properties in the (GeTe)1-(MnZnCdTe3)x system can be achieved by doping with the donor impurity Sb.

An important practical aspect of the fabrication of HPPs of a particular composition is the choice of appropriate technology and equipment. It is well known that not only the composition and total concentration of background impurities, but also distortions of the crystal lattice depend on this choice.

Traditional methods of forming multi-component coatings are characterized by preliminary production of material of the same composition with subsequent transfer to the surface of the product. This significantly complicates the process of coating formation and makes it inflexible due to the need to form coatings of different composition. Therefore, there is an urgent need to develop new technologies for the formation of multicomponent coatings.

One of the concepts for solving the mentioned problem is to use technologies based on simultaneous sputtering (co-sputtering) of individual components of the coating by corresponding controlled sources [6]. It should be noted that in recent years there has been a significant increase in interest in such technologies and corresponding equipment [7]. At the same time, when implementing any of the mentioned technologies, it is problematic to ensure the uniformity of the composition of the coating over the area of the product [8].

A natural way to solve this problem is to increase the number of sources of individual coating components while simultaneously reducing their size. However, a significant reduction in the size of traditional sources runs into fundamental limitations of both a physical and constructive character. So, the development of such a sputtering system for the formation of multi-component coatings, which on the one hand would have in its composition a sufficiently large number of independent sources of coating components, which sizes can be varied within wide limits, and on the other hand would provide the possibility of controlling the mode of operation of each of these sources is actual today.

A new ion-plasma sputtering system was created at Kharkiv National Aerospace University «Kharkiv Aviation Institute» [9], which is a type of inverse magnetron systems [10]. The system provides sputtering of a large number of target cathodes of a simple design, made of individual coating components. Due to the absence of fundamental restrictions on the size of target cathodes, there is a possibility of forming homogeneous coatings of almost any composition.

At the same time, our experience of operating the specified ion-plasma system indicates that the process of target cathodes sputtering with accelerated ions is affected by a number of interrelated parameters (electrical potentials on the electrodes of the sputtering system, current through the solenoids of the magnetic system, pressure of the plasma-forming gas, etc.). The consequence may be the sputtering of other structural elements of the technological chamber, and therefore uncontrolled alloying of the coating with additional components. Therefore, the objective of our work is to study the influence of metals from the composition of its structural elements on the structure and microhardness of WC coatings formed using a sputtering system.

Specimens and methods of research

Multicomponent coatings were formed on substrates made of 14X17 steel using inverse magnetron sputtering systems with a virtual anode, sectioned cathode assemblies with radial plasma flows. Segmented target cathodes made of pure tungsten and graphite were used to form tungsten carbide coatings. The thickness of the coatings was 3-6 microns.

The content of additional elements in the composition of the obtained coatings is due to the scattering of elements of the technological compartment, namely electrical screens. The sputtering process of these screens was controlled by changing the electrical potential on them during the formation of the coatings. The composition of the obtained coatings was studied using a scanning electron microscope REM-106.

X-ray structural analysis was performed on a DRON-4-07 diffractometer in copper Cu-Kα radiation using a nickel selective absorption filter. The rays reflected from the specimen were recorded by a scintillation detector. Instrumental conditions for recording diffractograms were the same for all specimens.

The diffractograms were subjected to standard processing (background separation, selection of the Kα1-doublet, approximation of the diffraction peaks by the pseudo-Voigt function), which is necessary for the calculation of the coatings structure parameters.

The calculation of the specimen's coherent-scattering region (CSR) was carried out according to Scherer's formula [11]

$$D = \frac{\lambda}{\beta \cos(\theta)}, \quad (1)$$

where D is the size of the CSR; λ –X-ray radiation wavelength; β – the actual physical expansion, and θ – the diffraction angle.

It should be noted that Scherer's formula gives an approximate size of the CSR, since it takes into account only the broadening of the diffraction peaks due to dimensional effects.

But since not all diffractograms have lines of two orders, the calculation was carried out by this method, and not by Williamson-Hall's [12].

The analysis was performed for the line due to the (111) plane. Annealed silicon powder had been used as a sample for determining instrumental line expansion.

Using the value of the integral half-width of the reference sample lines, we had obtained an instrumental function that has been used to extract the true expansion β from the total expansion of the specimen lines.

The microhardness of the specimens was measured using a PMT-3 microhardness tester, the weight of the load was 20 g.

Results and Discussion

The composition of the studied coating specimens is given in the table 1. From it, we can see that in addition to the main components of the coatings – W and C – a large number of other elements are observed in their composition, in particular: Fe, Mo, Cr, Ni, Ti and O. The content of the last component in the composition of the coatings is probably due to the adsorption of water vapor by the surface of the specimens during their fitting in the technological compartment of the electron microscope. At the same time, the absence of H in the composition of coatings can be explained by the low sensitivity of the microscope analyzer sensor to light elements.

According to the data presented in the table, the content of tungsten in the specimens varies widely. Moreover, as the content of this element decreases, the content of iron increases. At the same time, the chromium content does not change significantly from specimen to specimen. Nickel and titanium were found only in some specimens. It should be noted that the content of these two elements is relatively small.

In our opinion, the presence of Fe, Cr, Ni and Ti in the coatings is due to the fact that, in addition to the target cathodes, only electric shields made of 12X18N9T steel, which includes these elements, were sprayed in a controlled manner during the formation of the coatings.

Typical X-ray diffractogram for studied coatings is shown on Figure 1. According to the results of structural and substructural characteristics calculation, only cubic tungsten carbide WC (structural type B1, space group #225 [13]) with a rather small size of the DKR was found in the coatings. At the same time, in all specimens, the tungsten carbide lattice parameter significantly exceeds the value known from literary sources (a = 4.215Å [14]). Most likely, this is due to the presence of mechanical macrostresses in the coatings.

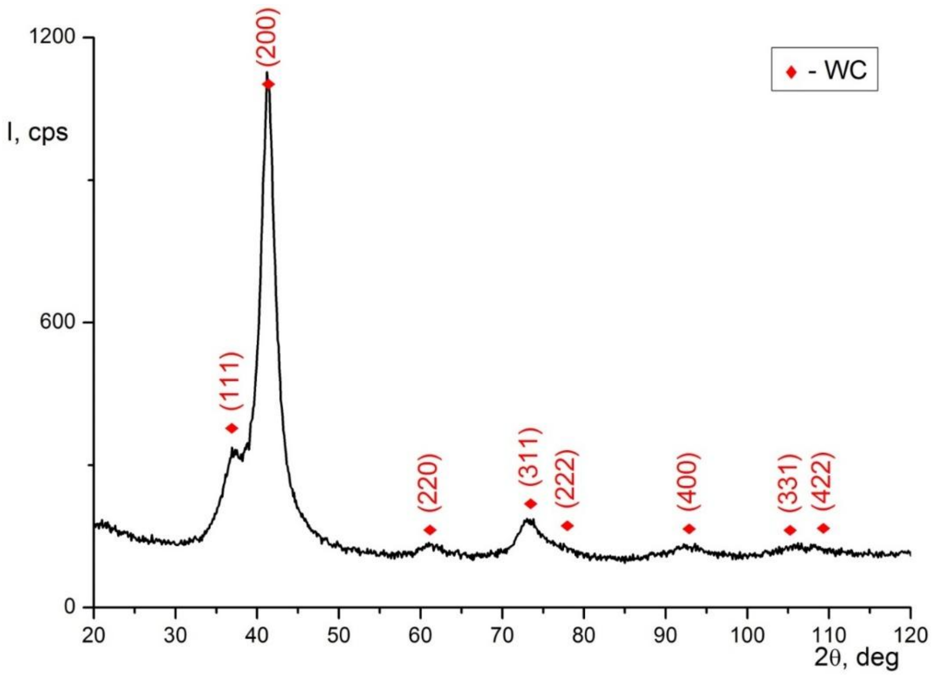

Fig. 1. Typical X-ray diffractogram for WC coatings

A comparative analysis of the CSR size, lattice period, and microhardness of coating specimens have shown (Fig. 2) that with an increase in the first parameter, there is a tendency for decrease of the other two. Moreover, the microhardness of one of the coating specimens reaches 17 GPa, which is a completely acceptable value for protective coatings based on tungsten carbide [15].

An important feature of the studied coating specimens is the presence of texture (200) in most of them. This is consistent with the results of our previous studies of WC coatings structure, which were also formed by the method of magnetron sputtering [16].

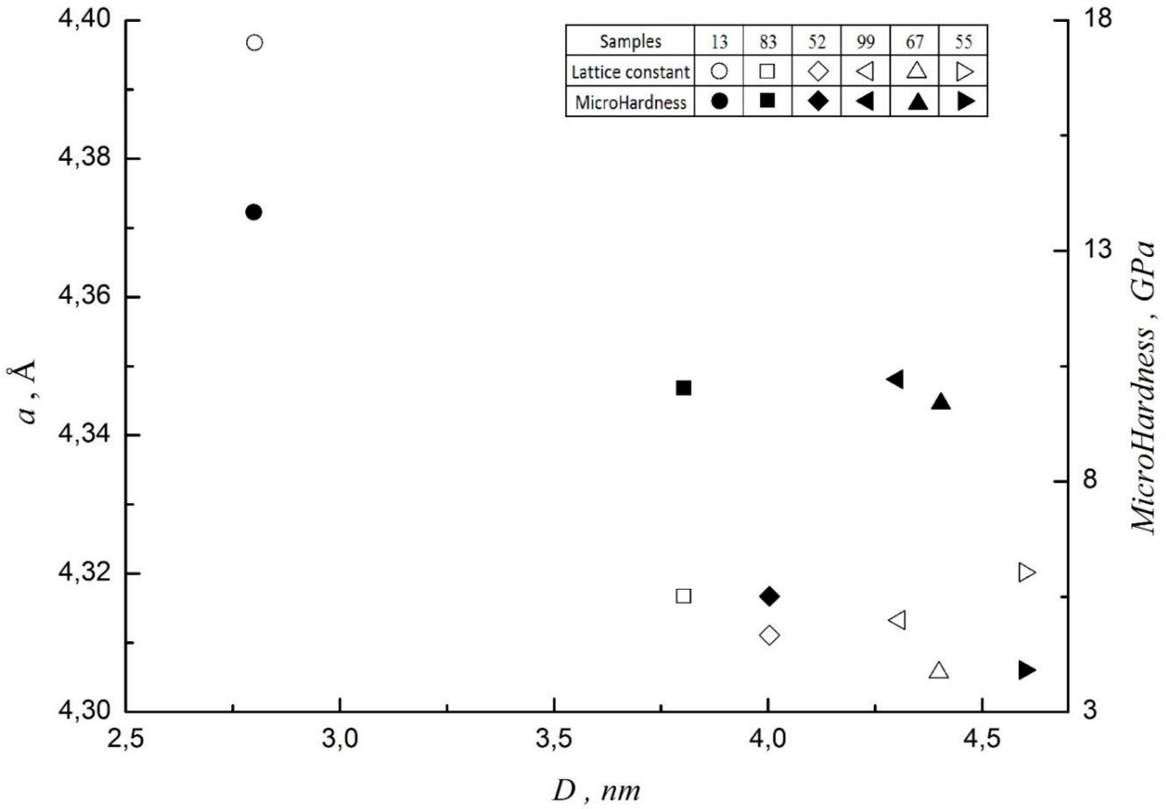

Fig. 2. Dependence of the lattice parameter and microhardness of WC coating specimens on the size of the co-herent-scattering region

Table 1

Content of elements in coating specimens

# of specimen	Mass content of elements in the coating, at. %								Microhardness,
	W	Fe	Mo	Cr	C	Ni	Ti	O	
13	75,6	6,5	9,2	1,3	4,8	-	-	2,6	17,5
67	72,4	6,9	11,9	1,2	4,5	-	2,8	0,3	5,0
83	68,6	8,6	11,9	1,4	4,3	-	3,2	2,0	5,5
52	63,7	15,2	9,3	4,8	4,2	1,6	-	1,2	4,7
99	61,8	15,2	10,8	3,1	4,3	0,9	3,4	0,5	3,9
55	43,5	32,1	5,9	9,8	2,9	4,1	-	1,7	6,0

The given data obviously testify to the determining influence not only of the composition, but also of significantly non-equilibrium formation conditions on the structure and microhardness of the investigated coatings. It is the non-equilibrium conditions of atoms condensation, the nature of their interaction both with each other and with the substrate that causes the appearance of texture [17] and the substructure of coatings. The point of the maximal weakening of impurities influence on the structure and mechanical properties of WC coatings requires further research.

Conclusions

As a result of additional sputtering of metals from the structural elements of the inverse magnetron sputtering system with sectioned cathode assemblies, multicomponent coatings based on tungsten carbide were formed. For the first time, the influence of the mentioned metals composition on the period of the crystal lattice, the size of X-rays coherents cattering region and the microhardness of coatings based on tungsten carbide have been determined. For the entire set of coating specimens, the specified parameters are related to each other. It is assumed that the listed features of the crystal structure and the presence of texture are determined not only by additional components in the composition of coatings, but also by significantly non-equilibrium conditions of their formation.

The obtained data, in our opinion, indicate the prospects of managing a wide range of physical and technical properties, including tribological, of multicomponent coatings based on tungsten carbide during their formation using inverse magnetron sputtering systems with sectioned cathode assemblies

References:

1. Huang Y., Zhi S., Zhang S., Yao W., Ao W., Zhang C., Liu F., Li, J. and Hu L. (2022). Regulating the Configurational Entropy to Improve the Thermoelectric Properties of (GeTe)1−x(MnZnCdTe3)x Alloys. Materials [Electronic resource]. 15(19), 6798. doi: 10.3390/ma15196798.

2. Li W., Xie D., Li D., Zhang Y., Gao Y. and Liaw P. K. (2021). Mechanical behavior of high-entropy alloys. Progress in Materials Science [Electronic resource]. 100777. doi: 10.1016/j.pmatsci.2021.100777.

3. Jiang B., Yu Y., Cui J., Liu X., Xie L., Liao J., Zhang Q., Huang Y., Ning S., Jia B., Zhu B., Bai S., Chen L., Pennycook S. J. and He J. (2021). Highentropystabilized chalcogenides with high thermoelectric perfor-mance. Science [Electronic resource]. 371(6531), 830–834. doi: 10.1126/science.abe1292.

4. Huang Y., Zhi S., Zhang S., Yao W., Ao W., Zhang C., Liu F., Li J. and Hu L., (2022). Regulating the Configurational Entropy to Improve the Thermoelectric Properties of (GeTe)1−x(MnZnCdTe3)x Alloys. Materials [Electronic resource]. 15(19), 6798. doi: 10.3390/ma15196798.

5. Xia M., Record M.C. and Boulet P. (2022). Investigation of pbsntese high-entropy thermoelectric alloy: A DFT approach. Materials [Electronic resource]. 16(1), 235. doi: 10.3390/ma16010235.

6. Yan X. H., Li J. S., Zhang W. R. and Zhang Y. (2018). A brief review of high-entropy films. Materials chemistry and physics [Electronic resource]. 210, 12–19. doi: 10.1016/j.matchemphys.2017.07.078.

7. Nagy P., Rohbeck N., Roussely G., Sortais P., Lábár J. L., Gubicza J., Michler J. and Pethö L. (2020). Processing and characterization of a multibeam sputtered nanocrystalline CoCrFeNi high-entropy alloy film. Surface and coatings technology [Electronic resource]. 386, 125465. doi: 10.1016/j.surfcoat.2020.125465.

8. Zhang W., Liaw P. K. and Zhang Y. (2018). Science and technology in high-entropy alloys. Science china materials [Electronic resource]. 61(1), 2–22. doi: 10.1007/s40843-017-9195-8.

9. Isakov A.V., Kolesnik V.P., Olhrimovskyy A.M., Stepanushkin N.P. and Taran A.A. Numerical simulation of abnormal glow discharge processes in crossed electric and magnetic fields. У: International Conference-School on Plasma Physics and Controlled Fusion and the Adjoint Workshop 'Nano- and microsized structures in plasmas', KhFTI NAS, Ukraine. С. 171–174.

10. Thornton J. A. (1978). Substrate heating in cylindrical magnetron sputtering sources. Thin solid films [Electronic resource]. 54(1), 23–31. doi: 10.1016/0040-6090(78)90273-0.

11. Vinila V. S., Isac J. Synthesis and structural studies of superconducting perovskite GdBa2Ca3Cu4O10.5+δ nanosystems. Design, Fabrication, and Characterization of Multifunctional Nanomaterials. 2022. P. 319–341. URL: https://doi.org/10.1016/b978-0-12-820558-7.00022-4.

12. Nath D., Singh F. and Das R., (2020). X-ray diffraction analysis by Williamson-Hall, Halder-Wagner and sizestrain plot methods of CdSe nano-particles- a comparative study. Materials chemistry and physics [Electronic resource]. 239, 122021. doi: 10.1016/j.matchemphys.2019.122021.

13. Cenzual, K., Gladyshevskii, R. and Villars, P., (2014). Handbook of inorganic substances. De Gruyter, Inc.

14. Shanenkov I., Nikitin D., Ivashutenko A., Rahmatullin I., Shanenkova Y., Nassyrbayev A., Han W. and Sivkov A. (2020). Hardening the surface of metals with WC1-x coatings deposited by high-speed plasma spraying. Surface and coatings technology [Electronic resource]. 389, 125639. doi: 10.1016/j.surfcoat.2020.125639.

15. Winarto W., Sofyan N. and Rooscote D. (2017). Porosity and wear resistance of flame sprayed tungsten carbide coatings/ GREEN PROCESS, MATERIAL, AND ENERGY: A SUSTAINABLE SOLUTION FOR CLIMATE CHANGE: Proceedings of the 3rd International Conference on Engineering, Technology, and Industrial Application (ICETIA 2016), Surakarta, Indonesia [Electronic resource]. doi: 10.1063/1.4985482.

16. Kolesnyk V. P., Chuhai O. M., Slyusar D. V., Kalakhan O. S., Voloshyn O. O., Oleinyk S. V. and Veselivs'ka H. H. (2019). Structure and properties of ionic plasma WC coatings. Materials science [Electronic resource]. 55(2), 220–224. doi: 10.1007/s11003-019-00292-1.

17. Bochulia T.V. and Sobol O.V. (2017). The use of structural engineering for obtaining superhard coatings based of nitrides transition metals. Machines. technologies. materials [Electronic resource]. 10(2), 77–83. https://stumejournals.com/journals/mtm/2017/2/77.full.pdf.

Надійшла до редколегії 12.10.2025

Відомості про авторів:

Слюсар Денис Віталійович – канд. техн. наук, Національний аерокосмічний університет «Харківський авіаційний інститут», доцент кафедри космічної техніки та нетрадиційних джерел енергії, Україна; e-mail: d.sliusar@khai.edu; ORCID: https://orcid.org/0000-0002-8314-6587

Чугай Олег Миколайович – д-р. техн. наук, Національний аерокосмічний університет «Харківський авіаційний інститут», професор кафедри фізики, Україна; e-mail: oleg.chugai@khai.edu; ORCID: https://orcid.org/0000-0002-2857-6592

Колодій Ігор Вікторович – Національний науковий центр "Харківський фізико-технічний інститут" (ННЦ ХФТІ), молодший науковий співробітник, Україна; ORCID: https://orcid.org/0000-0001-8598-9732

Олійник Сергій Володимирович – д-р. техн. наук, Національний аерокосмічний університет «Харківський авіаційний інститут», доцент кафедри фізики, Україна; e-mail: sergey.oliynick@khai.edu; ORCID: https://orcid.org/0000-0001-6073-8531

Полубояров Олексій Олександрович – канд. техн. наук, Національний аерокосмічний університет «Харківський авіаційний інститут», старший викладач кафедри фізики, Україна; e-mail: o.poluboiarov@khai.edu, ORCID: https://orcid.org/0000-0002-8587-8669

Волошин Юлія Андріївна – PhD**,** Національний аерокосмічний університет «Харківський авіаційний інститут», доцент кафедри радіоелектронних та біомедичних комп'ютеризованих засобів та технологій, Україна; e-mail: y.voloshyn@khai.edu; ORCID: https://orcid.org/0000-0003-4138-6731

Куліш Сергій Миколайович – канд. техн. наук, Національний аерокосмічний університет «Харківський авіаційний інститут», професор кафедри радіоелектронних та біомедичних комп'ютеризованих засобів та технологій, Україна; e-mail: s.kulish@khai.edu; ORCID: https://orcid.org/0000-0002-5506-2714